Studies on chemically synthesized $ZnFe_2O_4$ and $MnFe_2O_4$ thin films

For electrochemical supercapacitor application

A Synopsis submitted To

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For the degree of

Doctor of Philosophy in Physics

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Dayanand Science College, Latur

2022

Ph.D. Synopsis

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Abstract of proposed work plan/problem:

In the proposed research work, Chemical Spray Pyrolysis will be used to synthesize $ZnFe_2O_4$ and $MnFe_2O_4$ thin films on amorphous and fluorine doped tin oxide coated conducting glass substrates. XRD, SEM, FESEM, EDAX, UV-Vis spectroscopy, and DC electrical conductivity measurements will be used to investigate the structural, morphological, compositional, optical, and electrical properties of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films. Cyclic voltammograms, galvanostatic charge-discharge, and electrochemical impedance spectroscopy measurements will be used to investigate the electrochemical supercapacitor performance of the $ZnFe_2O_4$ and $MnFe_2O_4$ thin films.

1. Introduction

Over the past few years, our society is facing severe problems related to the small-scale energy storage. Energy storage components that are low weight, flexible, cost effective and environmentally friendly are required for portable electronic devices such as mobile phones, laptops, smart watches, and so on [1]. Because of their low cost and high performance, conventional capacitors and batteries have been widely used as energy storage devices. When it comes to the current energy demands of portable electronic gadgets, hybrid automobiles, and consumer electronics, energy storage technologies like conventional capacitors and batteries can't keep up. Furthermore, both conventional capacitors and batteries have notable advantages and disadvantages. Conventional capacitors have very high power densities and low energy densities as compared to batteries. In comparison to a conventional capacitor, a battery has a higher energy density and a lower power density [2]. With the rapid development of portable electronics devices, there has been an ever-increasing demand for alternative energy storage devices that can bridge the gap between conventional capacitor and battery, and have higher energy density, power density, long cycle life, and fast charge-discharge rates [3].

Supercapacitors have a higher energy density than conventional capacitors, a higher power density than batteries, quick charge-discharge rates, and a long cycle and shelf life. Supercapacitors have been widely used in portable electronic devices, memory backup systems, hybrid automobiles, and consumer electronics in place of batteries and conventional capacitors. The active material, substrate, and electrolyte employed in supercapacitors have a significant impact on their electrochemical performance [4].

The selection and preparation of electrode materials plays a crucial role in improving the performance of supercapacitors. Nanomaterials are the best candidates for enhanced ion adsorption or fast surface redox reactions. Metal oxides have extraordinary conductivities and specific capacitances, and therefore are considered appropriate for electrodes in high-energy and high-power supercapacitors. Specifically, transition metal oxides have been extensively studied for supercapacitor applications because they have multiple oxidation states and layered structures [5].

The bimetallic oxides spinel zinc ferrite ($ZnFe_2O_4$) and manganese ferrite ($MnFe_2O_4$) are encouraging materials for use in supercapacitor materials due to their low cost and environment friendliness as well as their electrical, optical and magnetic properties. They also exhibit different redox states and are electrochemically stable [6, 7].

In present study $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be deposited by using spray pyrolysis technique. The various film properties, like crystal structure, morphology, optical, electrical and electrochemical properties will be studied. The results obtained will be compared and discussed.

2. Review of Literature and Development in the Subject:

Doctor et al. [8] studied a facile fabrication of $ZnFe_2O_4$ coatings via electrophoretic deposition (EPD) methods Benefiting from systematic investigation for the deposition kinetic of ZnFe2O4 nanoparticles in the dispersion system of ethanol-acetylacetone with the addition of nitric acid, smooth $ZnFe_2O_4$ coating with good film characteristics was successfully and rapidly fabricated. With a preliminary study of $ZnFe_2O_4$ coatings as supercapacitor electrode, the specific capacitance decayed from 198 to 17.1 F g^{-1} when the deposition time increased from 0.5 to 10 min because of the poor electric conductivity.

Hussain et al. [9] studied role of nanotextured $ZnFe_2O_4/Fe_2O_3$ composite thin films fabricated by ultrasonic spray pyrolysis on the photoelectrochemical water oxidation reactions.

Lin and coworkers [10] prepared porous $ZnFe_2O_4$ (ZFO) by a template-assisted method. The ZFO precursor solution was impregnated into the hard-template polystyrene microspheres. Electrochemical tests show that the specific capacitance of the porous ZFO is 301.8 Fg^{-1} at the scan rate of 2 mVs^{-1} in 6 M KOH aqueous electrolyte. The porous ZFO displayed an excellent cycling stability in 6 M KOH aqueous electrolyte. Nearly 140.97% of its initial capacitance can be observed when the cycling current density is 2 A g^{-1} after the 5000 cycles.

Raut and colleagues [11] synthesized $ZnFe_2O_4$ thin film by a simple and low cost SILAR method without the use of surfactant or template. $ZnFe_2O_4$ solid-state symmetric supercapacitor device demonstrated voltage window of 1.0 V with specific capacitance of 32 Fg^{-1}, energy density of 4.47 $Whkg^{-1}$ and power density of 277 Wkg^{-1} at 1 Ag^{-1} current density. Such high performance capacitive behavior indicates $ZnFe_2O_4$ thin film is promising and low cost electrode material towards energy storage devices for various portable electronic systems.

Amulya et al. [12] assessed electrochemical characteristics of $MnFe_2O_4$ nanoparticles using various electrochemical techniques, including cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The dimensions in of the $MnFe_2O_4$ nanoparticles ranged from 16 to 24 nm. The specific capacitance values determined from the CV curves obtained using the $MnFe_2O_4$ versus Ag/AgCl electrodes at AC amplitude of 5 mV and in the frequency range from 1 Hz to 1 MHz in acidic and basic electrolytes with concentrations of 0.1 M were 4.2566 F g^{-1} and 2.2099 F g^{-1}, respectively.

Kuo and colleagues [13] have studied the formation of $MnFe_2O_4$ in a composite powder form. The electrochemical mechanism leading to the pseudocapacitance of $MnFe_2O_4$ in aqueous electrolyte solutions has been investigated. The ferrite crystallites, prepared by a solution method, contain Mn and Fe ions randomly distributed over the tetrahedral and octahedral sites of the spinel structure and exhibit an average capacitance exceeding 100 F/g-ferrite.

Akhlaghi and coworkers [14] reviewed the synthesis methods and physicochemical properties of $MnFe_2O_4$ nanoparticles. A comprehensive overview of

the latest and most promising researches on massive applications of $MnFe_2O_4$ -based nanostructures, including hyperthermia cancer therapy, magnetic resonance imaging (MRI), energy conversion and storage devices like Lithium-ion batteries and supercapacitors, as well as catalytic activities, sensors, hydrogen production, heavy metal removal, and drug delivery are presented.

Singh and Chandra [15] synthesized manganese nanoferrites via thermal decomposition method using metal organic precursors in organic solvent. The structural and optical properties of the nanoparticles were investigated. FTIR study validated the formation of spinel phase by showing its characteristic peaks at 593 cm^{-1} and 452 cm^{-1}. FESEM showed that the particles are spherical and the mean particle size ranged ~18.9 nm. Electrochemical performance of $MnFe_2O_4$ was evaluated using cyclic voltammetry (CV). The voltammograms were obtained using Pt as the working electrode within a potential range of -0.5 to +0.5 V at a scan rate of 50 mVs^{-1}.

3. Objectives of Research / proposed Hypothesis:

- To study synthesize of metal oxides such as $ZnFe_2O_4$ and $MnFe_2O_4$ in thin film form.
- To increase the surface area of active electrodes and hence to enhance the charge storing capacity of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films.
- To characterize $ZnFe_2O_4$ and $MnFe_2O_4$ thin films for structural, morphological, compositional and electrical properties.
- To study electrochemical properties such as cyclic voltammetry and galvanostatic charge-discharge of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films based supercapacitors.

4. Methodology to be adopted

There are various techniques available for deposition of thin films. Amongst these, the spray pyrolysis, which has the advantages of low cost, easy-to-use, safe and can be implemented in a standard laboratory, has been known to be suitable for many scientific studies and technological applications. This technique is based on the preparation of solutions of some salt of the material whose films are to be prepared. The chemical spray pyrolysis will be used to synthesize $ZnFe_2O_4$ and $MnFe_2O_4$ thin films. The work will performed in following manner:

a) Synthesis of Good Quality $ZnFe_2O_4$ and $MnFe_2O_4$ Thin Films

It is proposed to synthesize $ZnFe_2O_4$ and $MnFe_2O_4$ thin films by chemical spray pyrolysis. At initial stages the efforts will be done in order to deposit good quality $ZnFe_2O_4$ and $MnFe_2O_4$ thin films on amorphous and FTO coated conducting glass substrates. The various preparative parameters like concentration of precursor solution, thickness, substrate temperature, spray rate, carrier gas pressure, etc will be optimized to get good quality $ZnFe_2O_4$ and $MnFe_2O_4$ thin films. The as deposited films will be characterized by various characterization techniques.

b) Structural Studies

The as deposited $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be characterized by X-Ray diffraction (XRD) technique. The crystal structure, interplanar spacing, lattice planes, lattice parameters and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies

The morphology of the prepared $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be studied by using Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). The grain size, surface roughness, porosity will be studied. The compositional analysis of as deposited $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be studied by using Energy Dispersive Analysis by X-rays (EDAX) technique. The correlation between as taken composition and film composition will be obtained.

d) Optical Studies

The optical absorption of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be obtained by using UV-Vis (Ultraviolet-Visible) spectrophotometer. The coefficient of absorption, bandgap energy (Eg), nature of transition and power factor will be obtained from optical absorption spectra.

e) Electrical Studies

The electrical resistivity measurements of as deposited $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be carried out by using DC two point probe method. The room temperature electrical resistivity, type of conduction mechanism and activation energies will be determined.

f) Electrochemical Supercapacitor Studies

Performance of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance,

stability cycles and potential range. The supercapacitive performance of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be tested for symmetric and asymmetric modes, for achieving high power density. The galvanostatic charge-discharge mechanism will be studied using chronopotentiometry and the parameters such as specific capacitance, coulomb efficiency, specific energy, and specific power will be calculated. The electrochemical impedance spectroscopy analysis will be carried out in order to find the Rs and Rct values.

5. Importance of Study/Society Application

A modern technological society demands the use and storage of energy on a major scale, employing large and small system for that purpose. The energy stored in the capacitor is nonfaradaic electrical energy. No chemical changes are involved and hence cycle life of capacitor is unlimited. Super capacitors are maintenance free. Now a day's electrochemical capacitors or supercapacitors are used as storage devices to complement batteries. Supercapacitor have attracted more and more attention because of their advantages such as fast charging and discharging, long life span, simple principle and high power density compared with lithium batteries and traditional dielectric capacitors. Supercapacitors are used in particular, cars and trains, light weight electronic fuse, backup power sources for calculators, portable electronic devices, foldable electronic devices and wearable mobile phones.

6. Proposed Work Plan / Formulation and Structure of Study

Year wise plan of work and target to be achieved:

Plan of Work and Target to be achieved during First Year

During the first year all chemicals will be procured. A through literature survey will be done in order get good knowledge of metal oxides and supercapacitors. Efforts will be done in order to synthesize good quality $ZnFe_2O_4$ and $MnFe_2O_4$ thin films by using computerized spray pyrolysis. Various preparative parameters will be optimized.

Plan of Work and Target to be achieved during Second Year

In second year the $ZnFe_2O_4$ and $MnFe_2O_4$ thin films will be characterized by various techniques such as XRD, SEM, FESEM, AFM, TEM and EDAX, in order to study the structural, morphological and compositional properties. The films will be studied

for optical properties using UV-Vis spectrophotometer. The as grown films will be characterized by electrical resistivity measurement. Performance of $ZnFe_2O_4$ and $MnFe_2O_4$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and potential range. The results obtained will be discussed and interpreted. The two progress reports will be sent during the year. Two research papers will be communicated to the reputed journal at the end of this year.

Plan of Work and Target to be achieved during Third Year:

Results obtained in second year will be analyzed and published in reputed journals. Also the outcomes of our research work will be presented in national and international gatherings such as Seminars, Workshops, Exhibition and Conferences set during this year. Once this is done final synopsis will be submitted and after this thesis will be written. Thesis will be submitted to the university.

7. References

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Date: 24.03.2022

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